Synthetic Methods and Reactions; 40[1]. A General Ketone Synthesis by the Friedel-Crafts Acylation of Alkylsilanes

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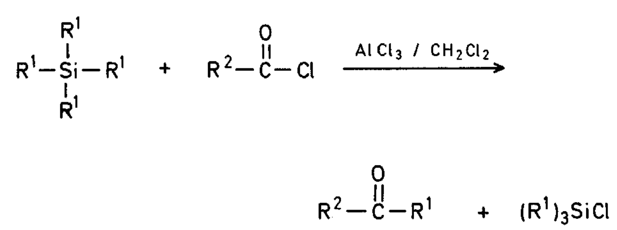
The Friedel-Crafts acylation reaction of arenes yields ketones, but the reaction so far was not found to be applicable to alkanes. Only lately have the electrofugal properties of silyl groups in allylsilanes been exploited in introducing allyl moieties into organic molecules[2–6] although activation of the C_β-X bonds by silicon had in fact been recognized[7] for some time. As allylsilanes are vinylogs of methylsilanes, the latter would be expected to transfer methyl (alkyl) groups to electrophiles, when proper experimental conditions are found. Electrophilysis[8] of C-Si bonds is also well known in the desilylative substitutions of aromatics[9] where initial attack of the electrophile is on the π-electron system.

The recently reported cyclopropyl ketone synthesis[10] by acylolysis of cyclopropyltrimethylsilane may not actually involve simple desilylative acylation, but could proceed via cleavage to alkyl 2-trimethylsilyl-4-chloropropyl ketones which then extrude chlorotrimethylsilane. This final step is analogous to that of cyclodestannylation of 4-tributylstannyl-1-butene[11]. Since cyclopropyl groups possess high π-character, this reaction[10] is thus more akin to the acyldesilylation of vinylsilanes[12] and alkynylsilanes[13].

So far no electrophilic acylolysis of alkylsilanes involving purely aliphatic C-Si bond reactions has been reported. This prompted us to investigate the feasibility of the Friedel-Crafts reaction of tetraalkylsilanes with acid chlorides and thereby to develop a general ketone synthesis. The choice of symmetrical silanes for our study was dictated by their ready availability and simplified product isolation.

The $AlCl_3$-catalyzed reaction of tetraalkylsilanes with acyl chlorides gives the corresponding ketones and trialkylchlorosilane. Data are summarized in the Table.



$$R^1_4Si + R^2-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{AlCl_3\ /\ CH_2Cl_2} R^2-\overset{O}{\overset{\|}{C}}-R^1 + (R^1)_3SiCl$$

The reaction is equally applicable to dialkyl, alkyl cycloalkyl, and alkyl aryl ketones. Alkoyl chlorides give higher yields than aroyl chlorides, reflecting the more delocalized nature and therefore weaker electrophilicity of the latter in their Friedel-Crafts complexes (or of the related acyl cations). Thus, we believe that this method furnishes a new, convenient method for the synthesis of ketones – in particular aliphatic ketones – starting from the desired acid chloride (either aliphatic or aromatic) and tetraalkylsilane in a single step.

Table. Ketone Synthesis by Acylation of Alkylsilanes

$(R^1)_4Si$	R^2—CO—Cl	R^1—CO—R^2	Yield [%][a]	b.p./torr	Lit. b.p./torr	m.p. of 2,4-DNP[b]	Lit. m.p. of 2,4-DNP
$(C_2H_5)_4Si$	C_2H_5—CO—Cl	C_2H_5—CO—C_2H_5	79	102–104°/760	102.7°/760[15]	154.2°	156°[17]
$(C_2H_5)_4Si$	*cyclo*-C_6H_{11}—CO—Cl	C_2H_5—CO—C_6H_{11}-*cyclo*	65	65–66°/5	65°/5[16]	145.8°	151°[16]
$(C_2H_5)_4Si$	C_6H_5—CO—Cl	C_2H_5—CO—C_6H_5	41	115–120°/21	115–120°/21[15]	186.5°	187–189°[18]
$(C_2H_5)_4Si$	*i*-C_3H_7—CO—Cl	C_2H_5—CO—C_3H_7-*i*	82	115–117°/760	114.5–115°/705[15]	109°	109–109.5°[19]
$(n-C_4H_9)_4Si$	C_2H_5—CO—Cl	*n*-C_4H_9—CO—C_2H_5	53	149–152°/760	149–150°/760[15]	79.5°	80–81°[17]
$(n-C_4H_9)_4Si$	*cyclo*-C_6H_{11}—CO—Cl	*n*-C_4H_9—CO—C_6H_{11}-*cyclo*	50	84–87°/3	85–86°/3[20]	70.2°	70–71°[20]
$(n-C_4H_9)_4Si$	C_6H_5—CO—Cl	*n*-C_4H_9—CO—C_6H_5	33	136–139°/25	135–140°/25[15]	167.8°	166°[17]

[a] Yield of isolated product.

[b] Recrystallized from ethanol.

General Procedure for Ketone Synthesis from Tetraalkylsilanes and Acid Chlorides:
To an ice-cooled, stirred solution of the freshly distilled acid chloride (25 mmol) and tetraalkylsilane (25 mmol) in dichloromethane (75 ml) is added anhydrous aluminum chloride (3.5 g, ~25 mmol). The mixture is allowed to warm to room temperature and then heated under reflux for 18 h, quenched with dilute hydrochloric acid, extracted, and the residual oil is purified through derivatization into Girad T adducts[14] and distilling the ketones obtained from the adducts. The ketones and their 2,4-DNPs give satisfactory analyses as well as physical and spectral properties identical with those reported (Table).

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[8] Electrophilysis is a general term for bond cleavage initiated by an electrophile which includes protolysis, nitrolysis, etc. Conversely, nucleophilysis is that initiated by a nucleophile, e.g. hydrolysis, aminolysis, etc.

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